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# ELECTRON DISPLACEMENT IN CARBON COMPOUNDS
# III. POLARITY DIFFERENCES IN CARBON-HYDROGEN UNIONS

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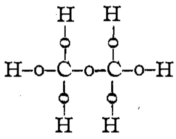
## General Discussion

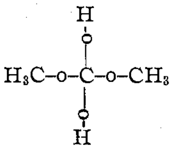
It is the purpose of this paper to demonstrate that the hypothesis of electron displacement[1] leads to the conclusion that the carbon-hydrogen unions in a paraffin hydrocarbon may be dissimilar in polarity, to explain how this dissimilarity can account for many phenomena of substitution, and to show experimentally that it can also account for the course of the reaction, when alkyl halides are converted into unsaturated hydrocarbons.

**Polarity Differences in Hydrocarbons.**—In methane the four electron pairs presumably are non-polar to the same extent and approximately equidistant from the carbon nucleus. In ethane the six electron pairs joining hydrogen to carbon are non-polar, and the pair joining the two carbon atoms is also non-polar, a condition best represented by formula I,[2]



$$H\text{-o-}\underset{\underset{H}{\circ}}{\overset{\overset{H}{\circ}}{C}}\text{-o-}\underset{\underset{H}{\circ}}{\overset{\overset{H}{\circ}}{C}}\text{-o-}H$$

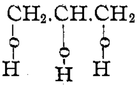
I



$$H_3C\text{-o-}\underset{\underset{H}{\circ}}{\overset{\overset{H}{\circ}}{C}}\text{-o-}CH_3$$

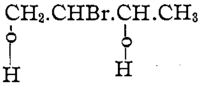
II

which indicates its symmetrical and non-polar character. In propane, however, due to the fact that hydrogen exerts a stronger pull on electrons than methyl does,[3] the electron pairs joining the central carbon to hydrogens are presumably not so firmly held by the carbon (Formula II) so that the polarities of all the carbon-hydrogen unions in propane are not the same, but differ as shown in Formula III.



$$\underset{\underset{H}{\circ}}{CH_2}.\underset{\underset{H}{\circ}}{CH}.\underset{\underset{H}{\circ}}{CH_2}$$

III



$$\underset{\underset{H}{\circ}}{CH_2}.CHBr.\underset{\underset{H}{\circ}}{CH}.CH_3$$

IV

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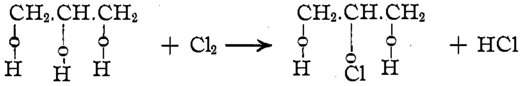
[1] Lucas and Jameson, THIS JOURNAL, **46,** 2478 (1924). Lewis, *ibid.*, **38,** 762 (1916).

[2] In order to avoid typographical difficulties in properly locating the electron pair, and at the same time preserve the familiar convention of lines representing bonds, we propose to use the symbol -o- to represent a single bond when it is in character non-polar, and to use the symbols o— and -o— to represent a single bond when there is a greater or less degree of electron displacement. Double and triple bonds may be represented in a similar manner.

[3] Thus, $K_A$ of formic acid is $2.14 \times 10^{-4}$ and of acetic acid is $1.8 \times 10^{-5}$; of malonic acid is $1.63 \times 10^{-3}$ and of isosuccinic acid is $8.6 \times 10^{-4}$; $K_B$ of ammonia is $1.8 \times 10^{-5}$ and of methyl amine is $5.0 \times 10^{-4}$.

As a result, hydrogen joined to a secondary carbon atom is more negative than hydrogen joined to a primary carbon, and likewise hydrogen joined to a tertiary carbon atom in a paraffin should be more negative than hydrogen joined to a secondary carbon.[4]

**Substitution Phenomena and Electron Displacement.**—Now, reaction takes place between chlorine and hydrocarbons for the same reason that chlorine reacts with hydrogen and with metals, that is, because molecular chlorine has a strong attraction for electrons; in other words, a high electron affinity.[5] In the reaction between a molecule of chlorine and one of methane to form methyl chloride and hydrogen chloride, each of the chlorine atoms in the resulting products more closely approximates the state of chlorine in the stable chloride ion, since the shared electron pair now holds either hydrogen or carbon, instead of the strongly electronegative chlorine. Likewise, in the reaction products from chlorine and any other hydrocarbon, the electron affinity of the chlorine atoms has been more or less completely satisfied. When an active chlorine molecule[6] approaches a propane molecule, the least firmly held electrons, that is, those joined to the central carbon atom, are most easily captured by the chlorine,[7] so that substitution takes place more easily on the secondary carbon atom, thus.



$$\underset{\underset{H}{\circ}}{CH_2}.\underset{\underset{H}{\circ}}{CH}.\underset{\underset{H}{\circ}}{CH_2} + Cl_2 \longrightarrow \underset{\underset{H}{\circ}}{CH_2}.\underset{\underset{Cl}{\circ}}{CH}.\underset{\underset{H}{\circ}}{CH_2} + HCl$$

Likewise, in a molecule of any other saturated hydrocarbon, the hydrogen atoms joined to secondary carbon atoms should be substituted more easily than those joined to primary, while those joined to tertiary carbon atoms should be substituted most easily of all. Results obtained by previous investigators are in substantial agreement with these statements: when chlorine reacts with *n*-pentane,[8] with *n*-hexane and with *n*-heptane,[9] and when bromine reacts with *n*-hexane,[10] the products formed are secondary halides mostly; when chlorine reacts with 2-methylpropane[11] and when bromine reacts with 2-methylbutane,[12] the main product is in each case a tertiary halide.

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[4] Likewise the halogen of tertiary halides should be more negative and therefore, in general, more reactive than the halogen of secondary and primary halides. Tertiary halides are the most reactive with alcoholic potassium hydroxide, but usually the least reactive in metathesis; compare Conant and Hussey, THIS JOURNAL, **47**, 476 (1925).

[5] Gerke, *ibid.*, **46**, 953 (1924).

[6] Lewis, *ibid.*, **38**, 775 (1916).

[7] If the electrons are rotating in orbits, they could be captured by a chlorine atom in passing through that part of the orbit lying near the latter.

[8] Schorlemmer, *Ann.*, **162**, 268 (1872).

[9] Schorlemmer, *Ann.*, **161**, 275 (1872). Michael and Turner, *Ber.*, **39**, 2154 (1906).

[10] Schorlemmer, *Ann.*, **188**, 250 (1877). Michael, *Ber.*, **34**, 4036 (1901).

[11] Butlerow, *Ann.*, **144**, 15 (1867).

[12] Poni, *Chem. Centralbl.*, **1906**, I, 442.

We are thus led to conclude that halogen reacts most easily with saturated hydrocarbons at the point where the electrons joining hydrogen and carbon are least firmly held by the carbon or, in other words, where the hydrogen atoms are most negative. This follows almost *a priori* from the fact that positive hydrogen, that is, ionizable hydrogen in acids, alcohols, etc., is rarely if ever substituted by halogens. This view of substitution is antagonistic to the prevailing ones,[13] according to which positive hydrogen is more easily substituted than negative hydrogen.

If the fundamental reaction is the attraction of halogen for electrons, then any other reagent which exerts a strong pull on electrons, such as concd. nitric and sulfuric acids, nitrosyl chloride and strong oxidizing agents, might react, especially at secondary or tertiary carbon atoms. Hydrocarbons containing tertiary carbon atoms are more easily nitrated,[14] and compounds with branched chains are more readily oxidized than normal chain compounds, while the action of nitrosyl chloride on normal paraffins appears to take place at secondary carbon atoms.[15]

**Unsaturated Hydrocarbons from Alkyl Halides.**—A difference in the polarity of carbon-hydrogen unions in alkyl halides might be expected to exert a directing influence upon the course of the reaction when hydrogen bromide is eliminated under the action of alcoholic potassium hydroxide.[16] For example, in 2-bromobutane, $CH_3CHBrCH_2CH_3$, it is necessary for this purpose to discuss only the relative polarities of the hydrogen atoms on C-1 and C-3. Writing the formula as $HCH_2CHBrCH_2CH_3$ it is at once apparent that we need to consider only the relative influences of hydrogen joined to C-1 and $CH_3$ joined to C-3. Since hydrogen has a greater attraction for electrons than methyl has, we may venture to say that C-1 exerts a stronger pull than C-3 does on the remaining electrons, so that those about C-1 are held somewhat more firmly than those about C-3. (Formula IV.)

Now, in discussing from an electron standpoint the mechanism by which hydrogen bromide is eliminated from 2-bromobutane, it is not necessary to consider the hydrogen atom except incidentally. It is reasonable to think that the reaction proceeds chiefly because bromine tends to go to its most stable form, that is bromide ion. To do so it must take with it not only the six unshared electrons in its shell but also two other shared electrons, a process which presumably can be accomplished most easily by the bromine appropriating the electron pair joining it to carbon. At the same time, the hydrogen atom would go with hydroxyl ion to form water, thus.

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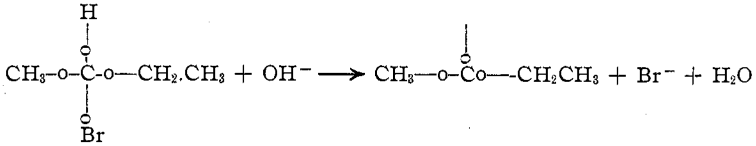
[13] Fry, *Z. physik. Chem.*, **76,** 388 (1911); THIS JOURNAL, **34,** 668 (1912); **36,** 248 (1914); **37,** 855 (1915). Stieglitz, *ibid.*, **44,** 1299 (1922).

[14] Brooks, "The Non-benzenoid Hydrocarbons," Chemical Catalog Co., **1922,** p. 60.

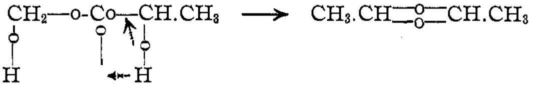
[15] Lynn, THIS JOURNAL, **41,** 368 (1919).

[16] The course of such a reaction might be influenced also by the tendency to form the more symmetrical compound.



$$CH_3\text{-o-}\underset{\underset{Br}{\overset{|}{o}}}{\overset{\overset{H}{|}}{\overset{o}{C}}}\text{-o—}CH_2.CH_3 + OH^- \longrightarrow CH_3\text{—o-}\overset{\overset{|}{o}}{Co}\text{—}CH_2CH_3 + Br^- + H_2O$$

This is essentially the course of the reaction as assumed by Nef. In the methylene derivative C-2 would be highly unsaturated, because there are only six electrons in its outer shell, and it would pull over an electron pair from either C-1 or C-3, in order to have a complete shell of eight electrons about it. But since C-1 exerts the greater attraction for electrons, the pair could move more easily from C-3, and the hydrogen nucleus would then move with the electron pair to C-2, so that



$$\underset{\underset{H}{|}}{\underset{o}{CH_2}}\text{—o-}\underset{\underset{|}{o}}{Co}\text{—}\underset{\underset{H}{|}}{\underset{o}{CH}}.CH_3 \longrightarrow CH_3.CH\text{=o=}CH.CH_3$$

the result of the reaction is 2-butene. The non-reversibility of a rearrangement of this type, so strongly emphasized by Nef, is at once apparent.

By a similar mechanism, the action of alcoholic potassium hydroxide on 2-bromopentane would produce 2-pentene, rather than 1-pentene. Since the same type of reaction takes place when an olefin is produced by the removal of water from a molecule of an alcohol, a similar explanation from the electronic standpoint is applicable, the intermediate compound of the methylene type rearranging to the corresponding unsaturated hydrocarbon. The dehydration of 2-butanol by means of phosphorus pentoxide[17] yields 2-butene exclusively, a result in harmony with the behavior of 2-bromobutane with alcoholic potassium hydroxide. However, since some acidic dehydrating agents, such as sulfuric acid may, by combining with the product, cause it to change to an isomeric form, it is felt that the behavior of alkyl halides in alcoholic potassium hydroxide is a more satisfactory reaction to study.

Our experiments show that from 2-bromobutane, 2-butene is practically the sole product, while from 2-bromopentane the resulting hydrocarbon is a mixture of approximately 70% of 2-pentene and 30% of 1-pentene.

## Experimental Part

### I. Alcoholic Potassium Hydroxide and 2-Bromobutane

**Butene from 2-Bromobutane.**—The 2-bromobutane prepared from 2-butanol,[18] b. p. 98–100°, and hydrobromic acid, distilled at 88.0–90.5° (uncorr.). Of the bromide, 65 g. (0.45 mole) was allowed to flow slowly into a solution of potassium hydroxide, 80 g. (1.4 mole) in 120 g. of alcohol, heated in an oil-bath at 125–130°. The gas evolved was passed through an inclined reflux condenser in order to condense the larger part of the alcohol, next through water to remove the remainder of the alcohol, then through a tube

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[17] Harries and Evers, *Ann.*, **390,** 238 (1912).

[18] Kindly furnished by the Standard Oil Co., of New Jersey.

containing anhydrous calcium chloride, then through a U-tube kept, by means of ice water, at a temperature of 2–5°, in order to condense out higher-boiling substances, of which there proved to be none, and finally into a flask containing 85 g. (0.47 mole) of bromine at —10–0°. To the flask were attached a dropping funnel, through which the bromine could be introduced, and two U-tubes in series, the first being kept below 0° in order to condense any butene that might not react, and the second containing carbon tetrachloride, which served the double purpose of catching any bromine fumes coming over, and of indicating changes of pressure within the system. The time required for a run was about three hours.

The crude dibromobutane was washed with approximately 2 *N* sodium hydroxide solution to remove the excess of bromine, then with water, and dried over anhydrous calcium chloride. Of the three experiments performed, the first and second were unsatisfactory because of losses due to mishaps, and the third was entirely satisfactory, giving 91.3 g. of crude dibromobutane, a yield of 89.0%.

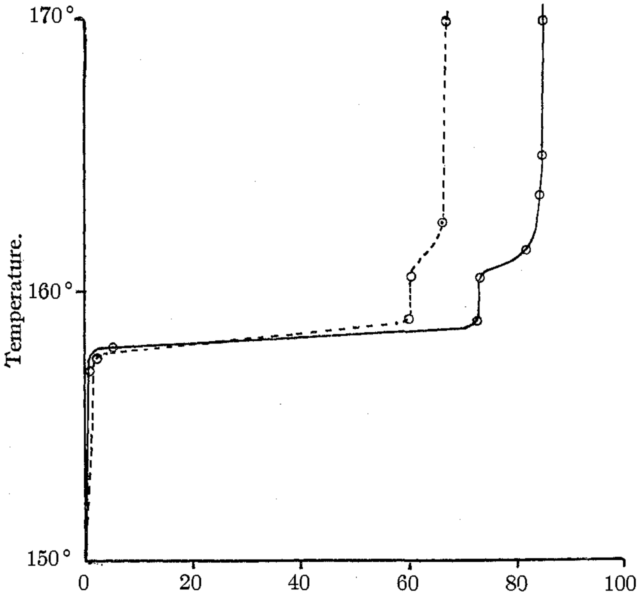

Fig. 1.—Fractional distillation of $C_4H_8Br_2$.
First and second runs combined – – – – – – third run ————.

**Separation of the Dibromobutanes.**—The two portions of crude dibromides, that is, the 70.2 g. from the first and second runs, and the 91.3 g. from the third run were separately subjected to a systematic fractional distillation in flasks of the Eastman type. The curve in Fig. 1 shows the separation effected after approximately six distillations. From the curves it is evident that there are two compounds present, one boiling at 157.8–159.0° (corr.) at 746 mm. and the other at 160.5–161.5°. Now, the *meso* form of 2,3-dibromobutane boils at 158°, and the racemic form[19] at 161°, while the boiling point of 1,2-dibromobutane[20] is 165.6–166° (755.5 mm.). Therefore the latter compound is

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[19] Wislicenus, Talbot and Henze, *Ann.*, **313,** 242 (1900).

[20] Wurtz, *Ann.*, **152,** 23 (1869). Compare Linnemann, *Ann.*, **161,** 199 (1872). Farvorsky and Sokownin. *Ann.*, **354,** 370 (1907).

not present in the mixture of dibromides, which is composed entirely of the *meso* and racemic forms of the 2,3-dibromide, resulting from the addition of bromine to the *cis* and *trans* forms of 2-butene, respectively. The action of alcoholic potassium hydroxide on 2-bromobutane, therefore, yields exclusively 2-butane, of which approximately 86% is the *cis* form and 14% the *trans* form.

**Dichlorobutanes from 2-Bromobutane.**—An experiment similar to the preceding was next carried out, except that the amount of 2-bromobutane was only 27 g., and chlorine, instead of bromine, was added to the 2-butene. The yield of crude dichlorobutane was 20.0 g., or 80.5% of that calculated. Fractional distillation of these chlorides in a manner similar to the preceding was not very satisfactory, probably because of the smaller amount of material. At the end of six fractionations, the following cuts were obtained: temperature range (corr.), 110.0–115.5°, 1.5 g.; 115.5–116.5°, 10.3 g.; 116.5–117.5°, 3.6 g.; 117.5–118.5°, 1.8 g.; 118.5–122.5°, 1.3 g.; 122.5–130.0°, 0.4 g.; residue, 1.0 g. The 10.3g. fraction distilling at 115.5–116.5° (corr.), which is 52% of the total product, is probably the *meso* form of 2,3-dichlorobutane.[21]

## II. Alcoholic Potassium Hydroxide and 2-Bromopentane

**Pentene from 2-Bromopentane.**—Pure 2-pentanol, b. p. 118–119° (corr.) at 745 mm., prepared from *n*-propyl bromide, b. p. 71–71.2°, magnesium and acetaldehyde by the method of Woods and Scarf,[22] gave with hydrobromic acid a bromide that when washed with cold, concd. sulfuric acid and water, and then dried with anhydrous potassium carbonate, distilled at 117–118° (corr.)[23] at 746 mm.; $n_D^{20} = 1.4415$. Repetition of the purification process did not change either value.

The 2-pentanol used for the following experiments was a commercial product,[18] whose purity was established by determining the purity of its bromide. The crude alcohol was dried with anhydrous potassium carbonate and distilled through a 60cm. Hempel column, and the part coming over at 116–117°, which constitute a 70% of the total, was considered to be pure 2-pentanol. It was converted into the corresponding bromide, which distilled at 117.5–118.5° (corr.) at 745 mm. after a purification treatment similar to that described; $n_D^{20} = 1.4416$. This result indicates that the alcohol used was practically free from 3-pentanol, an impurity which is undesirable, since the two alcohols as well as the two bromides[24] distil at practically the same temperature.

**Pentene from 2-Bromopentane.**—The conversion of 2-bromopentane into pentene was accomplished in a manner similar to the formation of butene, but in this case the composition of the product was established by adding hydrogen bromide instead of bromine to the unsaturated hydrocarbon, and determining the composition of the resulting mixture of monobromo-pentanes by means of fractional distillation and refractive indexes. 2-Bromopentane, 53 g. (0.35 mole), was dropped slowly into a boiling solution of 60 g. (1 mole) of potassium hydroxide in 90 g. of alcohol, heated in an oil-bath at 130–135°. The pentene evolved passed through an inclined reflux condenser at 40°, in order to condense most of the alcohol, and directly into a flask holding 100 cc. of xylene, b. p., 135–140°, and surrounded by ice. The xylene solution of the pentene was washed thrice with ice cold water in order to remove alcohol, dried with anhydrous potassium carbonate, and then distilled through a 50cm. Hempel column into a solution of 40 g. (0.5 mole) of hydrogen bromide in 60 g. of glacial acetic acid, kept cold by a freezing bath of ice and salt. The pentene distilled over the range of 35–42°, about one half

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[21] Scheschukow [*J. Russ. Phys.-Chem. Gess.*, **17,** 1509 (1885)] gives 115–120° as the boiling range of 2,3-dichlorobutane.

[22] Woods and Scarf, *J. Soc. Chem. Ind.*, **42,** 13T (1923).

[23] Wurtz [*Ann.*, **125,** 118 (1863)] gives the boiling point as 113°.

[24] Lucas and Moyse, This Journal, **47,** 1459 (1925).

at 36° and one fourth at 40°. Since the the boiling point of 2-pentene[25] is 36.4° and of 1-pentene[26] is 39–40°, the mixture appeared to have a composition of approximately 75% of 2-pentene and 25% of 1-pentene.

The increase in weight of the acetic acid was 18 g., indicating that the 3-bromopentane gave a 75% yield of pentenes. The reaction mixture was kept at 0° for two hours, then at 10–15° in the ice chest for 16 hours. It was poured into ice water and the resulting oily layer of crude bromides was washed twice with water and dried with anhydrous potassium carbonate. It weighed 35 g. (0.23 mole) corresponding to a 66% yield from the 3-bromopentane and 90% from the pentenes.

**Analysis of the Bromopentane Mixture.**—By means of fractional distillation, a separation can be made of 1-bromopentane, b. p. 128°, from a mixture of 2-bromopentane, b. p. 117.5–118.5°, and 3-bromopentane,[24] b. p. 118–118.2°, the composition of which mixture can be determined by means of the refractive index. Since we now know the ratio of these two bromides which result from the addition of hydrogen bromide to 2-pentene alone,[24] it is possible to calculate from the ratio of the bromides obtained in this experiment the proportion of 1-pentene and 2-pentene. The bromide mixture was slowly fractionated from a small flask with attached column of the Eastman type. A few drops of the liquid, probably unchanged pentene, distilled at a very low temperature; then no more came over until at 117° distillation of the main product began, and the temperature rose rapidly to 118°. Three fractionations gave 30 g., 117–118.5° (corr.); 2 g., 118.5–120° (corr.); 0.5 g., 120–125° (corr.); and 0.1 g., 125–129° (corr.). Assuming that one-half of the fraction, 120–125° is 1-bromopentane, the total yield of this product is 0.35 g., or 1%.

On redistilling the fraction 117–118.5°, the first few drops were discarded, so that practically the entire portion came over at 118.2–118.4° (corr.); $n_D^{20}$, 1.4426. The product was then washed thrice with ice-cold, concd. sulfuric acid in order to remove any alcohol, twice with water, dried with anhydrous potassium carbonate and then gave $n_D^{20} =$ 1.4429. After longer contact with the drying agent, the refractive index reached the constant value of 1.4431.

**Composition of the Pentene Mixture.**—Since pure 2-pentene and hydrogen bromide give a mixture of bromides, the refractive index of which is 1.4437, the hydrocarbon mixture must contain 28% of 1-pentene in order to give a product having a refractive index of 1.4431. But as the presence of a small amount of 1-bromobutane in the reaction product accounted for 1% of 1-butene, the composition of the hydrocarbon mixture obtained from 2-bromobutane by the action of alcoholic potassium hydroxide is 71% of 2-pentene and 29% of 1-pentene. Because of the limitations of the analytical procedure, the actual composition may vary as much as 15% from these values.

**Refractive Index of a Known Mixture of 2- and 3-Bromopentanes.**—The mean of five readings of the refractive index of a mixture composed of 2.00 g. of each of the two bromides was $n_D^{20} = 1.44294$, which checks with 1.44295, the mean as calculated. This indicates a linear relation between composition and refractive index.

**Stability of 2-Bromobutane at 140°.**—In view of the fact that alkyl bromides rearrange at elevated temperatures, it was desirable to study the rearrangement of 2-bromobutane at a temperature somewhat above its boiling point, in order to ascertain the possibility of its undergoing rearrangement during the process of fractional distillation. After 4 g. of 2-bromobutane had been heated for 13 hours at 140° in a sealed glass tube, no hydrogen bromide had been formed, and no change in the refractive index could be detected. This shows that there is no tendency for rearrangement to take

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[25] Risseghem, *Compt. rend.*, **158,** 1694 (1914).

[26] Brouchet, *Bull. soc. chim.* [3] **7,** 567 (1892).

place at that temperature, and that it is reasonable to assume that none took place during the process of distillation, at a lower temperature.

In conclusion, the helpful criticism of Dr. A. A. Noyes and of Dr. M. L. Huggins is gratefully acknowledged.

## Summary

1. The action of alcoholic potassium hydroxide on 2-bromobutane results in the formation of butenes consisting of approximately 86% of *cis*-2-butene and 14% of *trans*-2-butene and no 1-butene.

2. The action of alcoholic potassium hydroxide on 2-bromopentane results in the formation of pentenes consisting of approximately 71% of 2-pentene and 29% of 1-pentene.

3. An explanation of these phenomena is offered from the standpoint of electron displacement.

4. A new hypothesis of the mechanism of substitution processes is offered, which states that substitution takes place most easily at the point where electrons are least firmly held by carbon.

5. A new type of valence bond is proposed, by means of which the direction of electron displacements can be readily indicated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

# THE PREPARATION OF TRIARYLMETHYL ACETATES

BY C. S. SCHOEPFLE

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The only method which has been available for the preparation of triarylmethyl acetates is the reaction of silver acetate upon the triarylmethyl halides.[1] Acetic anhydride does not react with triaryl carbinols, and acetyl chloride or acetyl bromide gives the triarylmethyl chloride or bromide, respectively. It has now been found that silver acetate can be replaced to advantage by ammonium acetate. Triphenyl-bromomethane when shaken for ten hours with dry, finely divided ammonium acetate in benzene gives an almost quantitative yield of triphenylmethyl acetate (triphenyl-chloromethane reacts similarly but the reaction is much slower). Moreover, the acetate is formed when dry ammonia is passed into a solution of triphenyl-bromomethane to which a small amount of acetic acid has been added. Two products are possible in this case; the bromide may react with the ammonium acetate to give the acetate, or it may react with the excess ammonia to give the amine.

$$R_3C—Br + CH_3COONH_4 \longrightarrow R_3C—O—COCH_3 + NH_4Br \quad (1)$$

$$R_3C—Br + 2NH_3 \longrightarrow R_3C—NH_2 + NH_4Br \quad (2)$$

The first reaction proceeds with sufficient rapidity so that with an excess of acetic acid present, practically no amine is formed.

[1] Gomberg and Davis, *Ber.*, **36,** 3924 (1903).